

DESCRIPTION

TITLE OF THE INVENTION: RELEASE FILM FOR PRODUCTION OF
CERAMIC GREEN SHEET

TECHNICAL FIELD

[0001]

The present invention relates to a release film for production of a ceramic green sheet, and relates to a release film for production of a ceramic green sheet suppressing the corrosion of a release layer due to an organic solvent when a ceramic sheet is processed or an internal electrode is printed, to be free from an increase in a peeling force and the possibility of damaging the uniformity of peeling.

BACKGROUND ART

[0002]

Conventionally, a release film including a polyester film as a substrate and a release layer laminated on the polyester film has been used for forming a ceramic green sheet for a laminated ceramic capacitor or a ceramic substrate and the like. In recent years, the thickness of the ceramic green sheet has tended to also be reduced with reduction in the size of the laminated ceramic capacitor and an increase in the capacity thereof. The ceramic green

sheet is formed by applying a slurry containing a ceramic component such as barium titanate and a binder resin on a release film and drying the slurry. On the formed ceramic green sheet, an electrode is printed, and the ceramic green sheet is peeled off from the release film. Another ceramic green sheet is then laminated on the ceramic green sheet, followed by pressing, firing, and applying an external electrode, to produce a laminated ceramic capacitor. When a ceramic green sheet is formed on a release layer surface of a polyester film, minute projections on the release layer surface affect the formed ceramic green sheet. These are disadvantageously apt to cause defects such as repelling and pinholes. Therefore, a technique for achieving a release layer surface having excellent flatness has been developed (for example, see Patent Document 1).

[0003]

However, in recent years, the thickness of the ceramic green sheet has further been reduced, and a ceramic green sheet having a thickness of 1.0 μm or less, more specifically, 0.2 μm to 1.0 μm has been required. Therefore, a release film having a smoother release layer surface is desired. In addition, as the thickness of the ceramic green sheet is reduced, the strength of the ceramic green sheet is decreased, so that the ceramic green sheet is also desired to be peeled off from the release film in a

state where a peeling force is low and uniform. That is, it has become more important to minimize the force applied to the ceramic green sheet when the ceramic green sheet is peeled off from the release film so as not to damage the ceramic green sheet.

[0004]

In recent years, the use of a radical curable substance reacting under irradiation with active energy rays has been found to provide a smooth release layer surface. Simultaneously, a silicone-based component or its cured product contained in the release layer has been found to provide also excellent peelability from a ceramic sheet (for example, see Patent Document 2).

[0005]

However, the method described in Patent Document 2 is influenced by oxygen inhibition due to a radical polymerization reaction during processing in the air, which disadvantageously causes insufficient curing of the release layer surface. When the insufficient curing of the release layer surface occurs, the release layer is eroded by the organic solvent when the ceramic green sheet is processed and the internal electrode is printed, which impairs the increase in the peeling force and the uniformity of peeling. This has the possibility of damaging the ceramic green sheet during peeling.

[0006]

The radical polymerization reaction causes large curing shrinkage, to be disadvantageously apt to cause curl to occur in the release film. When curl occurs in the release film, the transportability of the release film is deteriorated, and the precision of electrode printing is reduced. These have the possibility of causing defects.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0007]

Patent Document 1: JP-A-2000-117899

Patent Document 2: International Publication No.
2013/145864

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0008]

The present invention, as a result of intensive studies in view of the above circumstances, provides a release film for production of a ceramic green sheet, which maintains high smoothness of a release layer surface, and which reduces and equalizes a force applied to the ceramic green sheet when the ceramic green sheet is released from a release film, thereby being free from the possibility of

damaging a ceramic green sheet during the removal from the release film, even when it is used for an ultrathin layer product having a thickness of 1 μm or less.

MEANS FOR SOLVING THE PROBLEMS

[0009]

That is, the present invention has the following configurations.

1. A release film for production of a ceramic green sheet,

the release film comprising:

a polyester film including a surface layer **A** substantially containing no inorganic particles; and

a release layer provided on the surface layer **A**,

wherein the release layer is obtained by curing a composition which contains a binder **A** containing a cationically curable substance, and one or more release agents **b**.

2. The release film for production of a ceramic green sheet according to the above 1, wherein an absolute value of a difference between a diiodomethane contact angle θ_1 of a release layer surface and a diiodomethane contact angle θ_2 of the release layer surface after being immersed in toluene is 3.0° or less.

3. The release film for production of a ceramic

green sheet according to the above 1 or 2, wherein at least one of the release agents **b** is a compound having a silicone skeleton.

4. The release film for production of a ceramic green sheet according to any one of the above 1 to 3, wherein the binder **A** containing the cationically curable substance is contained in an amount of 80% by mass or more based on a total solid content of the release layer.

5. The release film for production of a ceramic green sheet according to any one of the above 1 to 4, wherein the binder **A** containing the cationically curable substance contains at least one compound selected from a compound having an alicyclic epoxy group in its molecule and a compound having an oxetane ring in its molecule.

6. The release film for production of a ceramic green sheet according to any one of the above 1 to 5, wherein at least one of the release agents **b** is a silicone having an alicyclic epoxy group.

7. The release film for production of a ceramic green sheet according to any one of the above 1 to 6, wherein the release film has a release layer surface having average area surface roughness (Sa) of 7 nm or less, and a maximum protrusion height (P) of 100 nm or less.

8. A method for producing a ceramic green sheet having a thickness of 0.2 μm to 1.0 μm , wherein the release

film for production of a ceramic green sheet according to any one of the above 1 to 7 is used.

9. A method for producing a ceramic capacitor, wherein the method for producing a ceramic green sheet according to the above 8 is employed.

EFFECT OF THE INVENTION

[0010]

The present invention can provide a release film for production of a ceramic green sheet causing no corrosion of a release layer due to an organic solvent when a ceramic sheet is processed or an internal electrode is printed, to be free from an increase in a peeling force and the possibility of damaging the uniformity of peeling.

MODE FOR CARRYING OUT THE INVENTION

[0011]

The present inventors have found that, by using a polyester film which has controlled surface roughness and has one surface having a release layer provided thereon, the release layer containing a binder A containing a cationically curable substance, and one or more release agents b, a release film for production of a ceramic green sheet having excellent peelability can be provided, wherein the release layer is free from the possibility of being

eroded by an organic solvent. The present inventors have found that the use of a cationically curable substance having small curing shrinkage can provide a release film which is less likely to cause curl to occur and is free from the possibility of reducing the precision of electrode printing. Hereinafter, the present invention will be described in detail.

[0012]

It is preferable that a release film for production of a ceramic green sheet of the present invention has a surface layer A substantially containing no inorganic particles on at least one surface of the polyester film, and a release layer obtained by curing a composition which contains at least a binder A containing a cationically curable substance, and one or more release agents b is laminated on the surface layer A. The cationically curable substance is not subjected to curing inhibition due to oxygen, whereby the cationically curable substance is free from the possibility of causing insufficient curing of the release layer surface even in the air, and can suppress the corrosion of the release layer due to the organic solvent. The cationically curable substance has small curing shrinkage, whereby the cationically curable substance is less likely to cause curl to occur, and is free from the possibility of reducing the precision of electrode printing.

The cationically curable substance used here refers to a compound in which cations generated in a reaction system serve as active species to proceed a curing reaction.

[0013]

It is preferable that the release layer of the present invention is less likely to be corroded by the organic solvent. The corrosion of the release layer can be confirmed by evaluating a difference between the surface states of the release layer before and after the release film is immersed in the organic solvent. As the organic solvent used for the immersion, it is preferable to use toluene used for a general ceramic slurry, assuming a ceramic green sheet producing process. An example of a method for evaluating the surface state of the release layer is evaluation based on a contact angle. A change in the contact angle of the release layer surface before and after being immersed in toluene is preferably smaller.

[0014]

The type of droplet used for measuring the contact angle is not particularly limited, and water, bromonaphthalene, and ethylene glycol and the like can be suitably used, but diiodomethane capable of more remarkably observing the difference between the surface states of the release layer is most preferably used.

[0015]

As the absolute value of a difference ($\theta_1 - \theta_2$) between a diiodomethane contact angle θ_1 of the release layer surface and a contact angle θ_2 of the release layer surface after the release film is immersed in toluene at room temperature for 5 minutes is smaller when diiodomethane is used as the droplet used for measuring the contact angle, the solvent resistance of the release layer surface is excellent, which is preferable. Specifically, the absolute value is preferably 3.0° or less, more preferably 2.0° or less, and most preferably 1.0° or less. When the absolute value is 3.0° or less, the corrosion of the release layer due to the organic solvent when a ceramic green sheet is processed or an internal electrode is printed is suppressed. This is free from an increase in a peeling force and the possibility of damaging the uniformity of peeling, which is preferable. The difference ($\theta_1 - \theta_2$) between the diiodomethane contact angle θ_1 of the release layer surface and the contact angle θ_2 of the release layer surface after the release film is immersed in toluene at room temperature for 5 minutes is preferably smaller, and most preferably 0° . The absolute value of the difference may be 0.05° or more.

[0016]

(Polyester film)

Polyester constituting the polyester film used as a substrate in the present invention is not particularly

limited, and a film formed from polyester usually used generally as a release film substrate can be used. However, the polyester is preferably crystalline linear saturated polyester composed of an aromatic dibasic acid component and a diol component. For example, the polyester is more suitably polyethylene terephthalate, polyethylene-2,6-naphthalate, polybutylene terephthalate, polytrimethylene terephthalate, or a copolymer containing constituent components of these resins as main components. Above all, a polyester film formed from polyethylene terephthalate is particularly suitable. In the polyethylene terephthalate, the content of the repeating unit of ethylene terephthalate is preferably 90 mol% or more, and more preferably 95 mol% or more. Small amounts of other dicarboxylic acid component and diol component may be copolymerized with the polyethylene terephthalate. From the viewpoint of cost, the polyethylene terephthalate is preferably produced only from terephthalic acid and ethylene glycol. Known additives such as an antioxidant, a light stabilizer, an ultraviolet absorber, and a crystallization agent may be added as long as the effects of the release film of the present invention are not impaired. The polyester film is preferably a biaxially-stretched polyester film for reasons such as a high bidirectional elastic modulus.

[0017]

The intrinsic viscosity of the polyethylene terephthalate film is preferably 0.50 to 0.70 dl/g, and more preferably 0.52 to 0.62 dl/g. When the intrinsic viscosity is 0.50 dl/g or more, no breakage often occurs in a stretching step, which is preferable. Conversely, when the intrinsic viscosity is 0.70 dl/g or less, the cuttability of the film when being cut to a predetermined product width is good, and dimensional defects do not occur, which are preferable. It is preferable that raw materials are sufficiently dried in vacuum.

[0018]

The method for producing the polyester film of the present invention is not particularly limited, and methods generally used conventionally can be used. For example, the polyester film can be obtained by melting the polyester with an extruder, extruding the melted product into a film form, cooling the extruded product with a rotary cooling drum to obtain an un-stretched film, and biaxially stretching the un-stretched film. The biaxially-stretched film can be obtained by a method for sequentially biaxially stretching a longitudinally or transversely uniaxially stretched film in a transverse or longitudinal direction, or a method for simultaneously biaxially stretching an un-stretched film in longitudinal and transverse directions.

[0019]

In the present invention, a stretching temperature when the polyester film is stretched is preferably equal to or higher than the secondary transition point (T_g) of the polyester. The film is preferably stretched 1 to 8 times, particularly 2 to 6 times in each of the longitudinal and transverse directions.

[0020]

The polyester film preferably has a thickness of 12 to 50 μm , more preferably 15 to 38 μm , and still more preferably 19 to 33 μm . When the thickness of the film is 12 μm or more, the film is free from the possibility of being deformed by heat during film production, processing step, and forming, which is preferable. Meanwhile, when the thickness of the film is 50 μm or less, the amount of the film to be discarded after use is not extremely increased, which is preferable in order to reduce an environmental load.

[0021]

The polyester film substrate may be a single layer or a multilayer of two or more layers, but the polyester film substrate preferably has a surface layer A substantially containing no inorganic particles on at least one surface. A laminated polyester film having a multilayer structure of two or more layers preferably has a surface layer B capable of containing inorganic particles and the like on a surface

opposite to the surface layer A substantially containing no inorganic particles. When a layer on which the release layer is applied is an A layer; a layer located on an opposite side to the A layer is a B layer; and a core layer excluding the layers is a C layer, examples of the laminated structure include a laminated structure such as a release layer/A/B or a release layer/A/C/B as a layer configuration in a thickness direction. Of course, the C layer may have a plurality of layer structures. The surface layer B may contain no inorganic particles. In that case, a coat layer containing at least inorganic particles and a binder is preferably provided on the surface layer B in order to impart slipperiness for winding the film into a roll.

[0022]

In the polyester film substrate of the present invention, the surface layer A forming the surface on which the release layer is applied preferably contains substantially no inorganic particles. At this time, the average area surface roughness (Sa) of the surface layer A is preferably 7 nm or less. When Sa is 7 nm or less, pinholes and the like are less likely to occur when super-thin layer ceramic green sheets to be laminated are formed, which are preferable. The average area surface roughness (Sa) of the surface layer A can be said to be preferably

smaller, but the average area surface roughness may be 0.1 nm or more. Here, it is preferable that, when an anchor coat layer and the like to be described below is provided on the surface layer A, the coat layer preferably contains substantially no inorganic particles. The average area surface roughness (Sa) after the coat layer is laminated is preferably within the above range. In the present invention, "contain substantially no inorganic particles" means that the content of the inorganic particles is 50 ppm or less, preferably 10 ppm or less, and most preferably equal to or less than the detection limit when an inorganic element is quantified by fluorescent X-ray analysis. This is because, even if the inorganic particles are not positively added into the film, contamination components derived from foreign matters, and dirt attached to raw material resins, or lines or devices in film producing processes may be peeled off, and mixed into the film.

[0023]

In the polyester film substrate of the present invention, the surface layer B forming the surface opposite to the surface on which the release layer is applied preferably contains inorganic particles from the viewpoints of the slipperiness of the film and the ease of air release. In particular, it is preferable to use silica particles and/or calcium carbonate particles. The content of the

inorganic particles contained in the surface layer B is preferably 5000 to 15000 ppm in total of the inorganic particles. At this time, the average area surface roughness (Sa) of the film of the surface layer B is preferably in a range of 1 to 40 nm. More preferably, the average area surface roughness (Sa) is in a range of 5 to 35 nm. When the total content of silica particles and/or calcium carbonate particles is 5000 ppm or more, and the Sa is 1 nm or more, air can be uniformly released in the case where the film is wound into a roll, and the film has a good winding appearance and good flatness. Therefore, the film is suitable for producing the super-thin layer ceramic green sheet. When the total content of silica particles and/or calcium carbonate particles is 15000 ppm or less and the Sa is 40 nm or less, the aggregation of a lubricant is less likely to occur, and coarse projections cannot be formed, whereby the quality of the super-thin layer ceramic green sheet to be produced is stable, which is preferable.

[0024]

As the particles contained in the B layer, inactive inorganic particles and/or heat-resistant organic particles and the like can also be used in addition to silica and/or calcium carbonate. However, from the viewpoints of transparency and cost, silica particles and/or calcium carbonate particles are more preferably used. Another

examples of inorganic particles which can be used include alumina-silica composite oxide particles and hydroxyapatite particles. Examples of the heat-resistant organic particles include crosslinked polyacrylic particles, crosslinked polystyrene particles, and benzoguanamine-based particles. When the silica particles are used, porous colloidal silica is preferable. When the calcium carbonate particles are used, light calcium carbonate surface-treated with a polyacrylic acid-based polymer compound is preferable from the viewpoint of preventing the lubricant from falling off.

[0025]

The average particle diameter of the inorganic particles added to the surface layer B is preferably 0.1 μm or more and 2.0 μm or less, and particularly preferably 0.5 μm or more and 1.0 μm or less. When the average particle diameter of the inorganic particles is 0.1 μm or more, the slipperiness of the release film is good, which is preferable. The average particle diameter of 2.0 μm or less is free from the possibility of causing pinholes to occur in the ceramic green sheet due to coarse particles on the release layer surface, which is preferable.

[0026]

The surface layer B may contain two or more types of particles made of different materials. The surface layer B

may contain the same type of particles having different average particle diameters.

[0027]

It is preferable that, when the surface layer B does not contain particles, a coat layer containing particles on the surface layer B has slipperiness. The coat layer is not particularly limited, and the coat layer is preferably provided by in-line coating in which the coat layer is applied during the formation of the polyester film. When the surface layer B does not contain particles and a coat layer containing particles is provided on the surface layer B, the surface of the coat layer preferably has average area surface roughness (Sa) of 1 to 40 nm for the same reason as that of the above-mentioned average area surface roughness (Sa) of the surface layer B. More preferably, the average area surface roughness (Sa) is in a range of 5 to 35 nm.

[0028]

From the viewpoint of reducing the pinholes, it is preferable that a reused material or the like is not used in the surface layer A as a layer on which the release layer is provided, in order to prevent inorganic particles such as a lubricant from being mixed.

[0029]

The thickness ratio of the surface layer A as the

layer on which the release layer is provided is preferably 20% or more and 50% or less of the total thickness of the substrate film. When the thickness ratio is 20% or more, the surface layer A is less likely to be affected by the influence of the particles contained in the surface layer B and the like from the inside of the film, and the average area surface roughness Sa easily satisfies the above-mentioned range, which is preferable. When the thickness ratio is 50% or less of the total thickness of the substrate film, the use ratio of the reused material in the surface layer B can be increased, to reduce the environmental load, which is preferable.

[0030]

From the viewpoint of economic performance, for the layer other than the surface layer A (the surface layer B or the above-mentioned intermediate layer C), 50 to 90% by mass of film scraps or reused materials for PET bottles can be used. Even in this case, it is preferable that the type, amount, particle size, and average area surface roughness (Sa) of the lubricant contained in the layer B satisfy the above ranges.

[0031]

In order to improve the adhesion of the release layer or the like to be applied later, or in order to prevent charging, a coat layer may be provided on the surface of

the surface layer A and/or the surface layer B of the film before stretching or after uniaxial stretching in the film forming process, or the film may be subjected to a corona treatment or the like.

[0032]

(Release layer)

The release layer of the present invention is preferably obtained by curing a composition which contains at least a binder A containing a cationically curable substance, and one or more release agents b (an additive for imparting peelability). The binder A containing the cationically curable substance can be crosslinked to form a coating film having a high elastic modulus. The elastic modulus of the release layer is increased, whereby the release layer is not deformed and does not follow when being peeled off. The release layer is free from the possibility of damaging the ceramic green sheet, which is preferable.

[0033]

As long as the function of the present invention is not impaired, other components can be added in addition to the resin and the additive. Here, in the present invention, the cationically curable substance is considered to have a changed compound structure after being cured in the coating layer. However, it is extremely difficult to accurately

express and describe the changed structure itself resulting from the cationically curable substance. Therefore, as described above, "the release layer is obtained by curing a composition which contains a binder A containing a cationically curable substance, and one or more release agents b" is expressed.

[0034]

As the cationically curable substance used in the release layer of the present invention, general cationically curable substances can be used, and the cationically curable substance is not particularly limited. However, the cationically curable substance is preferably a vinyl ether compound or a cyclic ether compound, and among them, a compound containing an oxetane compound or an epoxy group is preferably used. Examples of the oxetane compound include aliphatic, aromatic, and alicyclic compounds. Examples of the compound having an epoxy group include glycidyl ether type, glycidylamine type, glycidyl ester type epoxys, and alicyclic epoxys. In particular, glycidyl ether type epoxy and alicyclic epoxy are preferable. It is most preferable to use alicyclic epoxy from the viewpoint of reactivity. Examples of the glycidyl ether type epoxy compound include aromatic glycidyl ethers represented by a bisphenol type epoxy resin and a cresol novolak type epoxy resin, and aliphatic glycidyl ethers represented by

hydrogenated A-type glycidyl ether and butyl glycidyl ether. Examples of the alicyclic epoxy include alicyclic epoxy into which an ester skeleton, a dicyclopentadiene skeleton, a fluorene skeleton, or an ϵ -caprolactone skeleton or the like is introduced. The alicyclic epoxy may have other skeletons.

[0035]

As the alicyclic epoxy compound, commercially available alicyclic epoxy compounds can also be used. Examples of the commercially available products include Cyclomer (registered trademark) M100 and Celoxide (registered trademark) 2000 (all manufactured by Daicel Corporation, monofunctional), Celoxides (registered trademark) 2021P and 2081 (all manufactured by Daicel Corporation, bifunctional), EPOLEAD (registered trademark) GT401 (manufactured by Daicel Corporation, tetrafunctional), and EHPE (registered trademark) 3150 (manufactured by Daicel Corporation, polyfunctional).

[0036]

As the oxetane compound, commercially available oxetane compounds can also be used. Examples of the commercially available products include Aron Oxetanes (registered trademark) OXT-101, 212 (all manufactured by Toagosei Co., monofunctional), OXT221, OXT-121 (all manufactured by Toagosei Co., bifunctional), ETERNACOLS

(registered trademark) EHO, OXMA (all manufactured by Ube Industries, monofunctional), OXTP, OXBP (all manufactured by Ube Industries, bifunctional).

[0037]

The number of cationically curable functional groups in the cationically curable substance is not particularly limited, and may be one or two or more. In order to increase the crosslinking density of the release layer to improve the solvent resistance, the number of the functional groups is preferably two or more. The introduction position of the cationically curable functional group may be at any position in a terminal, a side chain, or a straight chain. The cationically curable functional group shown here refers to a functional group which may be a cross-linking point in a cation curing reaction.

[0038]

One type of the cationically curable substances may be used, or two or more types thereof may be used in mixture. Although not particularly limited, the use of two or more cationically curable substances causes complexity of a polymer network chain after the reaction to increase the crosslinking density. This makes it possible to suppress the corrosion of the release layer due to the organic solvent, which is preferable.

[0039]

Two or more types of cationically curable substances having different numbers of functional groups are preferably used although not particularly limited by theory. The use of the cationically curable substances having different numbers of functional groups can effectively construct a polymer network to provide a release layer having a high crosslinking density. For example, a cationically curable substance having two functional groups is mixed with a polyfunctional cationically curable substance having three or more functional groups to cause a bifunctional cationically curable substance to construct a linear polymer. A trifunctional or more cationically curable substance can be introduced into a part of the polymer chains to form a crosslinked structure between polymer chains, whereby the crosslinking density can be improved.

[0040]

When two or more types of cationically curable substances are used, the optimal ratio of the cationically curable substances is preferably 0.1 parts by mass or more and 50 parts by mass or less of one of the curable substances based on 100 parts by mass of the other curable substance, more preferably 0.5 parts by mass or more and 20 parts by mass or less, and most preferably 1 part by mass

or more and 10 parts by mass or less. When the amount of one of the curable substances is 0.1 parts by mass or more, the amount of the other curable substance incorporated into the crosslinked structure is not extremely reduced. This sufficiently provides an effect of increasing the crosslinking density, which is preferable. When one of the curable substances is used in an amount of 50 parts by mass or less, the crosslinked structures of the respective curable substances do not become dominant, whereby a complex polymer net chain obtained by mixing is formed to provide an effect of increasing the crosslinking density, which is preferable.

[0041]

The release layer of the present invention preferably has an increased crosslinking density in order to suppress the corrosion of the release layer due to the organic solvent. Therefore, any of a polymer, an oligomer, and a monomer may be used as the cationically curable substance. In particular, the use of the monomer makes it possible to increase the number of cross-linking points per given mass to increase the crosslinking density, which is preferable.

[0042]

In the release layer of the present invention, the cationically curable substance is preferably contained in an amount of 80% by mass or more and 99.9% or less based on

the solid content of the entire release layer, more preferably 90% by mass or more and 99.9% or less, and still more preferably 95% by mass or more and 99.9% or less. The release layer contains the cationically curable substance
5 in an amount of 80% by mass or more, whereby a cationic polymerization reaction can provide a high crosslinking density. This can suppress the corrosion of the release layer due to the organic solvent, which is preferable. At this time, the solid content of the entire release layer is
10 expressed as the total value of the solid contents of the binder component and the release agent since an acid generating agent is decomposed in a drying step or under irradiation of active energy rays, which makes it difficult to accurately calculate the minute mass of the acid
15 generating agent residue remaining in the release layer.

[0043]

(Acid generating agent)

It is preferable to use an acid generating agent in the release layer of the present invention in order to
20 cause a cationic polymerization reaction to proceed. The acid generating agent to be used is not particularly limited, and general acid generating agents are used. The use of a photo acid generating agent which generates an acid under irradiation with active energy rays makes it
25 possible to suppress an amount of heat during processing,

which is preferable. The use of a general acid such as a sulfonic acid type or a carboxylic acid type can also provide a release layer having a high crosslinking density suppressing the corrosion by the organic solvent. The use of the general acid requires a high processing temperature, and causes the possibility of roughening the release layer surface due to the heat shrinkage of the raw material film and deterioration in smoothness thereof. In addition, a metal salt type acid generating agent, a phosphoric acid ester type acid generating agent, and a block type acid generating agent in which an acid site is blocked can also be used. But the photo acid generating agent is most preferably used from the viewpoint of the amount of heat during processing for the aforementioned reason.

[0044]

As the photo acid generating agent, salts composed of onium ions and non-nucleophilic anions are suitably used from the viewpoint of reactivity. An organometallic complex represented by an iron arene complex or a carbocation salt represented by tropylium may be used, or an anthracene derivative or a phenol substituted with an electron-withdrawing group, for example, pentafluorophenol may be used.

[0045]

When the salts composed of onium ions and non-

nucleophilic anions are used as the photo acid generating agent, for example, iodonium, sulfonium, and ammonium can be used as the onium ions. As the organic group of the onium ions, triaryl, diaryl (monoalkyl), monoaryl (dialkyl), and trialkyl may be used. Benzophenone or 9-fluorene may be introduced, or other organic groups may be used. As the non-nucleophilic anions, it is suitable to use hexafluorophosphate, hexafluoroantimonate, hexafluoroborate, or tetra(pentafluorophenyl)borate. Tetra(pentafluorophenyl)gallium ions or anions obtained by replacing some of fluorine anions with perfluoroalkyl groups or organic groups may be used, and other anion components may be used.

[0046]

When the photo acid generating agent is used, the addition of a sensitizer makes it possible to improve the reactivity of the polymerization reaction to further suppress the corrosion of the release layer due to the organic solvent. The sensitizer is not particularly limited, and general sensitizers may be used, but an anthracene derivative and a naphthalene derivative are suitable. One or two or more of the sensitizers may be used.

[0047]

The amount of the photo acid generating agent to be

added to the coating solution is preferably 0.1 to 10 parts by mass based on the total mass of the binder A containing the cationically curable substance and the release agent b contained in the release layer. The amount is more preferably 0.5 to 8 parts by mass. The amount is still more preferably 1 to 5 parts by mass. When the amount is 0.1 parts by mass or more, the amount of an acid to be generated is sufficient. This is free from the possibility of insufficient curing, which is preferable. When the amount is 10 parts by mass or less, the amount of an acid to be generated is appropriate. This can suppress the amount of transition of the acid to the ceramic green sheet to be formed, which is preferable.

[0048]

The amount of the sensitizer to be added is preferably 0.1 to 5 times of the mass of the photo acid generating agent. The amount is more preferably 0.1 to 2 times. The amount of more than 0.1 times is free from the possibility of providing an insufficient sensitizing effect, which is preferable. When the amount is smaller than 5 times, the absorption of the active energy rays of the photo acid generating agent is inhibited. This is free from the possibility of insufficiently generating an acid, which is preferable.

[0049]

(Release agent b)

As the release agent b (additive for imparting releasability) used in the release layer of the present invention, silicone-based additives and non-silicone-based additives such as long-chain alkyl-based and fluorine-based additives, and the like can be used. It is preferable to use silicone-based additives from the viewpoint of peelability.

[0050]

The silicone-based additive is a material based on polyorganosiloxane having an organic group attached to a siloxane bond. The silicone-based additive is not particularly limited as long as the effects of the present invention can be obtained, and general silicone-based additives can be used. An acrylic resin or alkyd resin or the like having polyorganosiloxane in its side chain can also be used. Among the polyorganosiloxanes, polydialkylsiloxane can be suitably used, and among them, polydimethylsiloxane is more preferably used. Polydimethylsiloxane partially having a functional group is more preferable. The polydimethylsiloxane has the functional group, whereby an intermolecular interaction between a cationically curable substance and a hydrogen bond or the like is likely to be exhibited, to cause difficult transition of the component to the ceramic green

sheet, which is preferable.

[0051]

The functional group introduced into polydimethylsiloxane is not particularly limited, and may be a reactive functional group or a non-reactive functional group. The functional group may be introduced into one terminal, both terminals, or a side chain of polydimethylsiloxane. The functional group may be introduced into one position or each of a plurality of positions.

[0052]

As the reactive functional group to be introduced into polydimethylsiloxane, a cyclic ether group, a hydroxy group, a mercapto group, a carboxyl group, a methacryloyl group, and an acryloyl group and the like can be used. Although not particularly limited, it is preferable to use a cyclic ether group. In particular, when a cationically curable functional group such as a glycidyl ether group, an alicyclic epoxy group, or an oxetane ring is contained, the cationically curable functional group is incorporated into the crosslinked structure of the cationically curable substance. This causes difficult transition of the cationically curable functional group to the ceramic green sheet, which is preferable. Among them, when an alicyclic epoxy group is contained, the alicyclic epoxy group has

excellent compatibility with a binder component, whereby peelability is likely to be developed, which is most preferable. As the non-reactive functional group, a polyether group, an alkyl group, a fluoroalkyl group, a long-chain alkyl group, an ester group, an amide group, and a phenyl group and the like can be used.

[0053]

More specifically, a silicone-based additive having a cationically curable reactive group is preferably used, and a silicone-based additive having an epoxy group is more preferably used. It is most suitable to use a silicone-based additive having an alicyclic epoxy group as the epoxy group. More specifically, the structure of the silicone-based additive having an alicyclic epoxy group is described as follows: polydimethylsiloxane containing an alicyclic epoxy group or an acrylic resin having polydimethylsiloxane and an alicyclic epoxy group in a side chain is given as an example.

[0054]

The silicone-based additive used in the present invention is not particularly limited, and existing silicone-based additives can be used. Examples of commercially available products of silicones having a reactive functional group include X-22-170DX, X-22-3710, X-22-176DX, X-22-167B (all manufactured by Shin-Etsu Chemical

Co., Ltd.), and BYK-UV3500, BYK-UV3505, and BYK-UV3575 (all manufactured by BYK Chemie Japan). Examples of commercially available products of silicone-based additives having a cationically curable functional group include X-22-173BX, X-22-173DX, X-22-4741, and X-22-9002 (all manufactured by Shin-Etsu Chemical Co., Ltd.). Among them, X-22-169B, KF-102, X-62-7629, X62-7660, and X-62-7622 (all manufactured by Shin-Etsu Chemical Co., Ltd.) which are commercially available products of silicones having an alicyclic epoxy group, UV9300, UV9315, and UV9430 (all, manufactured by Momentive Performance Materials, Inc.), and Silcoleases (registered trademark) UV Poly200, 201, 215 (all manufactured by Arakawa Chemical Industries) and the like can be suitably used.

[0055]

The fluorine-based additive is not particularly limited, and existing fluorine-based additives can be used. For example, a fluorine-based additive having a perfluoro group and a fluorine-based additive having a perfluoroether group can be suitably used. Examples of commercially available products include Megaface (registered trademark) (manufactured by DIC Corporation), Optool (registered trademark) (manufactured by Daikin Industries), and Fclear (registered trademark) (manufactured by Kanto Denka Kogyo Co., Ltd.).

[0056]

As the long-chain alkyl-based additive, a long-chain alkyl-modified resin can be used, and a long-chain alkyl-based additive having an alkyl group having about 8 to 20 carbon atoms in its side chain such as polyvinyl alcohol and an acrylic resin is preferable. A copolymer which is a polymer having a (meth)acrylic acid ester as a main repeating unit, and contains a long-chain alkyl group having 8 to 20 carbon atoms in a transesterified portion can also be suitably used. Examples of commercially available products include Pyroyl (registered trademark) 1010, Pyroyl (registered trademark) 1050, and Pyroyl (registered trademark) 1070 (all, Lion Specialty Chemicals, Inc.), and Tesfine (registered trademark) 305 and Tesfine (registered trademark) 314 (all manufactured by Hitachi Chemical Co., Ltd.).

[0057]

Two or more of the release agents may be used in mixture, and at least one release agent is preferably a silicone-based additive, more preferably a silicone having a cationically curable functional group, and most preferably a silicone having an alicyclic epoxy group. At least one release agent is a silicone-based additive, whereby a release layer having excellent peelability is provided, which is preferable.

[0058]

The release layer of the present invention preferably contains the release agent b in an amount of 0.1% by mass or more and 20% by mass or less based on the solid content of the entire release layer. The amount is more preferably 0.5% by mass or more and 10% by mass or less, and still more preferably 0.5% by mass or more and 5% by mass or less. When the content is more than 0.1% by mass, releasability is imparted. This is free from the possibility of deteriorating the peelability of the ceramic green sheet, which is preferable. When the content is less than 20% by mass, a decrease in an intermolecular interaction with the cationically curable substance is suppressed. This is free from the possibility of causing transition of the release agent to the ceramic green sheet, which is preferable. At this time, the solid content of the entire release layer is expressed as the total value of the solid contents of the binder component and the release agent since an acid generating agent is decomposed in a drying step or under irradiation of active energy rays, which makes it difficult to accurately calculate the minute mass of the acid generating agent residue remaining in the release layer.

25 [0059]

The release layer of the present invention can contain particles having a particle size of 1 μm or less,

but from the viewpoint of the occurrence of pinholes, it is preferable that the release coating layer does not contain components forming protrusions such as particles, except for extremely few impurities which are unintentionally and undesirably mixed. It is particularly preferable that the release layer does not contain inorganic particles and organic particles regardless of the type, particle size, shape, solubility, or non-solubility of the particles.

[0060]

Additives such as an adhesion improver and an anti-static agent may be added to the release layer of the present invention as long as the effect of the present invention is not impaired. In order to improve the adhesion to the substrate, it is also preferable that the surface of the polyester film is subjected to a pretreatment such as anchor coating, a corona treatment, a plasma treatment, or an atmospheric pressure plasma treatment before providing the release coating layer.

(Features of release layer)

[0061]

In the present invention, the thickness of the release layer may be set according to the purpose of use, and is not particularly limited. The thickness of the release coating layer after curing is preferably 0.01 to 1.0 μm , more preferably 0.01 to 0.5 μm , still more

preferably 0.01 to 0.2 μm , and most suitably 0.02 to 0.1 μm . If the thickness of the release layer is more than 0.01 μm , sufficient peeling performance is obtained, which is preferable. If the thickness is 1.0 μm or less, curl defects are less likely to occur, and the amount of irradiation of active energy rays and the amount of heat required for curing are not increased. This is free from the possibility of causing a decrease in a processing speed, which is preferable also from the economical aspect.

[0062]

The release layer surface of the release film of the present invention is desirably flat so as not to cause defects in the ceramic green sheet coated and formed thereon. It is preferable that the average area surface roughness (S_a) is 7 nm or less. It is more preferable that the S_a is satisfied and the maximum protrusion height (P) of the release layer surface is 100 nm or less. It is particularly preferable that the average area surface roughness (S_a) is 5 nm or less and the maximum protrusion height is 80 nm or less. If the area surface roughness is 7 nm or less, and the maximum protrusion height is 100 nm or less, the defects such as pinholes do not occur when the ceramic green sheet is formed, and the yield is good, which is preferable. It can be said that the average area surface roughness (S_a) is preferably smaller, but the

average area surface roughness may be 0.1 nm or more, or 0.3 nm or more. It can be said that the maximum protrusion height (P) is also preferably smaller, but the maximum protrusion height may be 1 nm or more, or 3 nm or more.

[0063]

In the release film of the present invention, a peeling force when the ceramic green sheet is peeled off is preferably 0.5 mN/mm² or more and 3.0 mN/mm² or less. More preferably, the peeling force is 0.8 mN/mm² or more and 2.5 mN/mm² or less. If the peeling force is 0.5 mN/mm² or more, the peeling force is not too light. This is free from the possibility of causing the ceramic green sheet to float during transportation, which is preferable. The peeling force of 3.0 mN/mm² or less is free from the possibility of causing the ceramic green sheet to be damaged during peeling, which is preferable.

[0064]

The curl of the release film of the present invention after heating at 100°C for 15 minutes without applying tension is preferably 3 mm or less, and more preferably 1 mm or less. Of course, it is also preferable that the release film does not curl at all. The curl of 3 mm or less can provide less curl when the ceramic green sheet is formed and an electrode is printed, to improve the precision of printing, which is preferable.

(Method for forming release layer)

[0065]

In the present invention, the method for forming the release layer is not particularly limited, and the following method is used. A coating solution in which a composition containing a releasable resin and the like is dissolved or dispersed is spread on one surface of the polyester film of the substrate by coating and the like. A solvent and the like is removed by drying, followed by heat drying the coating solution. The dried product is then cured by irradiation with active energy rays or heat.

[0066]

When the coating solution is cured using the photo acid generating agent, a heating temperature is preferably 50°C or higher and 110°C or lower, and more preferably 60°C or higher and 100°C or lower. A heating time is preferably 30 seconds or less, and more preferably 20 seconds or less. When the temperature is 110°C or lower, the thermal load on the film is suppressed; the appearance defect such as heat shrinkage of the film is not easily caused; and the thickness of the ceramic green sheet is less likely to be uneven, which is preferable. When the temperature is 100°C or lower, the thermal load on the film is further reduced, and the film can be processed without impairing the flatness of the film, to further reduce the possibility of

causing the uneven thickness of the ceramic green sheet, which is particularly preferable. When the temperature is higher than 50°C, a diluting solvent used during coating is sufficiently dried. This is free from the possibility of causing process contamination or the like, which is preferable.

[0067]

As the active energy rays used for reacting the cationically curable substance using the photo acid generating agent, ultraviolet rays, electron beams, and X-rays and the like can be used, but ultraviolet rays are likely to be used, which are preferable. The integrated amount of light of ultraviolet rays with which cationically curable substance is irradiated is preferably 10 to 1000 mJ/cm², more preferably 15 to 500 mJ/cm², and still more preferably 15 to 100 mJ/cm². By setting the amount of light to 10 mJ/cm² or more, the curing of the resin sufficiently proceeds, which is preferable. By setting the amount of light to 1000 mJ/cm² or less, the speed during processing can be improved, whereby the release film can be economically prepared, which is preferable.

[0068]

In the present invention, the surface tension of the coating solution when the release layer is coated is not particularly limited, but it is preferably 30 mN/m or less.

By setting the surface tension as described above, the coatability after coating is improved, which can provide reduced unevenness of the surface of the coating film after drying.

[0069]

In the present invention, the coating solution when the release coating layer is coated is not particularly limited, but it is preferable to add a solvent having a boiling point of 90°C or higher. The addition of a solvent having a boiling point of 90°C or higher makes it possible to prevent bumping during drying, to level the coating film, and to improve the smoothness of the surface of the coating film after drying. The addition amount thereof is preferably about 10 to 80% by mass with respect to the whole coating solution.

[0070]

As the coating method of the coating solution, any known coating methods can be applied. For example, conventionally known methods such as a roll coating method (such as a gravure coating method or a reverse coating method), a bar coating method (such as a wire bar), a die coating method, a spray coating method, and an air knife coating method can be utilized.

<Examples>

[0071]

Hereinafter, the present invention will be described in detail with reference to Examples, but the present invention is not limited to the following Examples. Characteristic values used in the present invention were evaluated using the following methods.

[0072]

(Intrinsic viscosity of polyester resin (dl/g))

Based on JIS K 7367-5, measurement was performed at 30°C using a mixed solvent of phenol (60% by mass) and 1,1,2,2-tetrachloroethane (40% by mass) as a solvent.

[0073]

(Thickness of substrate film)

Using Millitron (electronic microindicator), four 5 cm square samples were cut from any four locations on a film to be measured.

Each of the samples was measured at 5 points (20 points in total), and the average value of the measurements was taken as a thickness.

[0074]

(Film thickness of release layer)

The cross-section of the release film cut into any size was observed with a transmission electron microscope, and the calculated value was taken as the thickness of the release layer.

[0075]

(Surface roughness)

The surface roughness is represented by values measured under the following conditions using a non-contact surface shape measurement system (VertScan R550H-M100, manufactured by Ryoka Systems Inc.). For average area surface roughness (S_a), the average value of five measurements was employed. For a maximum protrusion height (P), seven measurements were performed, and the maximum value of five measurements excluding the maximum and minimum values was used.

(Measurement conditions)

- Measurement mode: WAVE mode
- Objective lens: 10x
- 0.5×Tube lens
- Measurement area 936 μm × 702 μm

(Analysis conditions)

- Surface correction: 4th order correction
- Interpolation processing: Complete interpolation

[0076]

(Contact angle)

Using a contact angle meter (automatic contact angle meter DM-701, manufactured by Kyowa Interface Science Co., Ltd.) under conditions of 25°C and 50% RH, droplets of diiodomethane (droplet volume: 0.9 μL) were prepared on the release surface of the left release film standing still,

and the contact angles thereof were measured. As the contact angle, a contact angle after 30 seconds after each solution was dropped onto the release film was employed. The average value of five measurements was employed.

[0077]

(Contact angle after being immersed in toluene)

The release film used for the measurement was cut into a size of 5 cm × 5 cm, and immersed in a glass tray containing 30 mL of toluene at a liquid temperature of 25°C for 5 minutes with the release surface facing down. The immersed release film was taken out, air-dried for 15 minutes with the release surface facing up, and then vacuum-dried at 25°C overnight. The obtained release film after being immersed in toluene was measured by the same method as the method for measuring the contact angle.

[0078]

(Evaluation of change in contact angle)

When the diiodomethane contact angle of an initial release layer surface before being immersed in toluene measured by the method was θ_1 , and the diiodomethane contact angle of the release layer surface after being immersed in toluene was θ_2 , the absolute value of $\theta_1 - \theta_2$ was taken as a value of a change in the contact angles before and after being immersed in toluene. The change in the contact angle was evaluated according to the following

criteria.

Very good: $|\theta_1 - \theta_2| < 1.0^\circ$

Good: $1.0^\circ \leq |\theta_1 - \theta_2| < 2.0^\circ$

Average: $2.0^\circ \leq |\theta_1 - \theta_2| \leq 3.0^\circ$

Poor: $|\theta_1 - \theta_2| > 3.0^\circ$

[0079]

(Evaluation of pinholes of ceramic green sheet)

The compositions containing the following materials were stirred and mixed, and the mixture was dispersed for 30 minutes using a bead mill with 0.5 mm zirconia beads as a dispersion medium to obtain a ceramic slurry.

Toluene: 76.3 parts by mass

Ethanol: 76.3 parts by mass

Barium titanate (HPBT-1, manufactured by Fuji Titanium Industry Co., Ltd.): 35.0 parts by mass

Polyvinyl butyral: 3.5 parts by mass

(S-LEC (registered trademark) BM-S, manufactured by Sekisui Chemical Co., Ltd.)

DOP (dioctyl phthalate): 1.8 parts by mass

Then, the slurry was coated on the release surface of the obtained release film sample using an applicator such that the thickness after drying was 0.8 μm , and dried at 90°C for 1 minute. Then, the release film was peeled off to obtain a ceramic green sheet.

In the central region of the obtained ceramic green

sheet in the film transverse direction, light was applied from the opposite surface of the coating surface of the ceramic slurry in a range of 25 cm², and the occurrence status of pinholes viewed from the transmission of light was observed. The pinholes were visually determined according to the following criteria. Five measurements were performed, and the average value thereof was employed.

Very Good: No occurrence of pinholes

Good: Almost no occurrence of pinholes (target: pinholes of 2 or less per measurement area)

Average: Occurrence of pinholes (target: pinholes of 5 or less per measurement area)

Poor: Occurrence of a large number of pinholes
[0080]

(Evaluation of peelability of ceramic green sheet)

The compositions containing the following materials were stirred and mixed, and the mixture was dispersed for 60 minutes using a bead mill with 0.5 mm zirconia beads as a dispersion medium to obtain a ceramic slurry.

Toluene: 38.3 parts by mass

Ethanol: 38.3 parts by mass

Barium titanate (HPBT-1, manufactured by Fuji Titanium Industry Co., Ltd.): 64.8 parts by mass

Polyvinyl butyral: 6.5 parts by mass

(S-LEC (registered trademark) BM-S, manufactured by

Sekisui Chemical Co., Ltd.)

DOP (dioctyl phthalate): 3.3 parts by mass

Then, the slurry was coated on the release surface of the obtained release film sample using an applicator such that the thickness after drying was 10 μm , and dried at 90°C for 2 minutes to form a ceramic green sheet on the release film. The obtained release film including the ceramic green sheet was statically eliminated using a static eliminator (SJ-F020, manufactured by Keyence Corporation), and then peeled off at a width of 30 mm, a peel angle of 90°, and a peel speed of 10 m/min using a high-speed peeling tester (TE-701, manufactured by Tester Sangyo). The release film was peeled off in a direction in which the release film surface was pulled in a state where the surface of the ceramic green sheet was fixed. A stress applied during peeling was measured, and taken as a peeling force.

[0081]

(Evaluation of curl of release film)

The release film sample was cut into a size of 10 cm $\times$ 10 cm, and heat-treated in a hot-air oven at 100°C for 15 minutes without tension being applied to the release film. Thereafter, the release film sample was taken out of the oven, and cooled to room temperature. The release film sample was then placed on a glass plate with the release

surface facing upward. A height from the glass plate to the top of each corner at this time was measured, and the curl property was evaluated in accordance with the following criteria.

Very good: The sum of the corner portions was 1 mm or less.

Good: The sum of the corner portions was more than 1 mm and 3 mm or less.

Average: The sum of the corner portions was more than 3 mm and 10 mm or less.

Poor: The sum curl of the corner portions was more than 10 mm.

[0082]

(Preparation of polyethylene terephthalate pellets (PET (I)))

As an esterification reactor, a continuous esterification reactor including a three-stage complete mixing tank including a stirrer, a partial condenser, a raw material charging port, and a product outlet was used. The amount of TPA (terephthalic acid) was set to 2 tons/hour, and the amount of EG (ethylene glycol) was set to 2 mol per 1 mol of TPA. The amount of antimony trioxide was set such that the amount of Sb atoms with respect to produced PET was set to 160 ppm. These slurries were continuously supplied to a first reaction can of the esterification

reactor, and reacted at normal pressure at 255°C for an average residence time of 4 hours. Next, the reaction product in the first esterification reaction can was continuously taken out of the system, and supplied to a second esterification reaction can. 8% by mass of EG distilled off from the first esterification reaction can with respect to produced PET was supplied into the second esterification reaction can. Furthermore, an EG solution containing magnesium acetate tetrahydrate set such that the amount of Mg atoms with respect to the produced PET was set to 65 ppm and an EG solution containing TMPA (trimethyl phosphate) set such that the amount of P atoms with respect to the produced PET was set to 40 ppm were added, and they were reacted at 260°C at normal pressure for an average residence time of 1 hour. Then, the reaction product of the second esterification reaction can was continuously taken out of the system, and supplied to a third esterification reaction can. 0.2% by mass of porous colloidal silica having an average particle size of 0.9 μm after a dispersion treatment with the average number of treatments of 5 passes under pressure of 39 MPa (400 kg/cm²) using a high pressure disperser (manufactured by Nippon Seiki Co., Ltd.), and 0.4% by mass of synthetic calcium carbonate having an average particle size of 0.6 μm obtained by attaching 1% by mass of a polyacrylic acid

ammonium salt per calcium carbonate were added as 10% EG slurries, and they were reacted at 260°C at normal pressure for an average residence time of 0.5 hours. The esterification reaction product produced in the third esterification reaction can was continuously supplied to a three-stage continuous polycondensation reaction apparatus to perform polycondensation. The polycondensation product was filtered with a filter obtained by sintering stainless steel fibers having a 95% cut diameter of 20 μm , and then subjected to ultrafiltration. Then, the filtered product was extruded into water, cooled, and then cut into a chip shape to obtain a PET chip having an intrinsic viscosity of 0.60 dl/g (hereinafter abbreviated as PET (I)). The content of the lubricant in the PET chip was 0.6% by mass.

[0083]

(Preparation of polyethylene terephthalate pellets (PET (II)))

Meanwhile, a PET chip having an intrinsic viscosity of 0.62 dl/g and containing no inorganic particles made of calcium carbonate and silica and the like was obtained (hereinafter abbreviated as PET (II)) according to the above production of the PET chip.

[0084]

(Production of laminated film X1)

These PET chips were dried, then melted at 285°C,

melted at 290°C by a separate melt extruder, and subjected to two-stage filtration of a filter obtained by sintering stainless steel fibers having a 95% cut diameter of 15 µm and a filter obtained by sintering stainless steel particles having a 95% cut diameter of 15 µm, and merged in a feed block. The PET (I) and the and PET (II) were laminated such that the PET (I) was a surface layer B (opposite side layer to a release surface) and the PET (II) was a surface layer A (release surface side layer), extruded (cast) into a sheet shape at a speed of 45 m/min, and electrostatically adhered and cooled on a casting drum at 30°C by an electrostatic adhesion method, to obtain an un-stretched polyethylene terephthalate sheet having an intrinsic viscosity of 0.59 dl/g. The layer ratio was adjusted such that PET (I)/ PET (II) = 60%/40% was set in the calculation of the discharge amount of each extruder. Then, this un-stretched sheet was heated with an infrared heater, and then stretched by 3.5 times in a longitudinal direction at a roll temperature of 80°C according to the speed difference between rolls. Thereafter, the sheet was guided to a tenter, and stretched by 4.2 times in a transverse direction at 140°C. Then, a heat treatment was performed at 210°C in a heat fixation zone. Thereafter, a 2.3% relaxation treatment was performed at 170°C in a transverse direction to obtain a biaxially-stretched

polyethylene terephthalate film X1 having a thickness of 31 μm . Sa of the surface layer A of the obtained film X1 was 2 nm, and Sa of the surface layer B was 28 nm.

[0085]

(Production of laminated film X2)

A thickness was adjusted by changing a speed during casting without changing the same layer configuration and stretching condition as those of the laminated film X1, to obtain a biaxially-stretched polyethylene terephthalate film X2 having a thickness of 25 μm . In the obtained film X2, Sa of a surface layer A was 3 nm, and Sa of a surface layer B was 29 nm.

[0086]

(Laminated film X3)

As a laminated film X3, E5101 (Toyobo Co., Ltd. Ester (registered trademark) film, manufactured by Toyobo Co., Ltd.) having a thickness of 25 μm was used. E5101 has a structure in which inorganic particles are contained in the film. Sa of a surface layer A of the laminated film X3 was 24 nm, and Sa of a surface layer B was 24 nm.

[0087]

<Example 1>

A coating solution having the following composition was coated on a surface layer A of a laminated film X1 using a wire bar such that the film thickness of a release

layer after drying was 50 nm, and dried at 90°C for 15 seconds. The coating solution was then irradiated with ultraviolet rays using an ultraviolet ray irradiator (LC6B, H-bulb, manufactured by Heraeus Co., Ltd.) such that the integrated amount of light was 70 mJ/cm² to obtain a release film for production of a super-thin layer ceramic green sheet. A ceramic slurry was applied to the obtained release film, and the surface roughness, peelability, change in a contact angle after being immersed in toluene, pinholes, and curl and the like of the release layer were evaluated, and good evaluation results were obtained.

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:

3',4'-epoxycyclohexylmethyl 3,4-

epoxycyclohexanecarboxylate: 0.90 parts by mass

(Product name: Celloxide (registered trademark) 2021P, manufactured by Daicel Corporation, solid content: 100% by mass, bifunctional)

Release agent b: Alicyclic epoxy group-containing polydimethylsiloxane:

0.10 parts by mass

(Product name, UV Poly215, manufactured by Arakawa Chemical Industries, solid content: 100%)

Acid generating agent: Boron-based cationic curing UV

catalyst: 0.26 parts by mass

(Product name: UV CATA 211, active ingredient: 19% by mass, manufactured by Arakawa Chemical Co., Ltd.)

[0088]

<Example 2>

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the coating solution was changed to a coating solution having a composition shown below.

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:

Celloxide (registered trademark) 2021P: 0.86 parts by mass

Butanetetracarboxylic acid tetra (3,4-epoxycyclohexylmethyl)modified ϵ -caprolactone: 0.04 parts by mass

(Product name: EPOLEAD (registered trademark) GT401, manufactured by Daicel Corporation, solid content: 100%, tetrafunctional)

Release agent b: UV Poly215: 0.10 parts by mass

Acid generating agent: UV CATA211 (active ingredient: 19% by mass):

0.26 parts by mass

[0089]

(Example 3)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the coating solution was changed to a coating solution having a composition shown below.

(Coating solution 3)

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:

Celloxide (registered trademark) 2021P: 0.63 parts by mass

EPOLEAD (registered trademark) GT401: 0.27 parts by mass

Release agent b: UV Poly215: 0.10 parts by mass

Acid generating agent: UV CATA211 (active ingredient: 19% by mass): 0.26 parts by mass

[0090]

(Example 4)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the coating solution was changed to a coating solution having a composition shown below.

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:

Celloxide (registered trademark) 2021P: 0.45 parts by mass

EPOLEAD (registered trademark) GT401: 0.45 parts by mass

Release agent b: UV Poly215: 0.10 parts by mass

Acid generating agent: UV CATA211 (active ingredient: 19% by mass): 0.26 parts by mass

[0091]

(Example 5)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the coating solution was changed to a coating solution having a composition shown below.

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:

Celloxide (registered trademark) 2021P: 0.86 parts by mass

2-ethylhexyl oxetane: 0.04 parts by mass

(Product name: Aron Oxetane (registered trademark) OXT-221, manufactured by Toagosei Co., Ltd., solid content: 100% by mass, bifunctional)

Release agent b: UV Poly215: 0.10 parts by mass

Acid generating agent: UV CATA211 (active ingredient: 19% by mass): 0.26 parts by mass

[0092]

(Example 6)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the coating solution was changed to a coating solution having a composition shown below.

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:

EPOLEAD (registered trademark) GT401: 0.90 parts by mass

Release agent b: UV Poly215: 0.10 parts by mass

Acid generating agent: UV CATA211 (active ingredient: 19% by mass): 0.26 parts by mass

[0093]

(Example 7)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the coating solution was changed to a coating solution having a composition shown below.

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:

Polyfunctional alicyclic epoxy group-containing polymer: 0.90 parts by mass

(Product name: EHPE (registered trademark) 3150,
manufactured by Daicel Corporation, solid content: 100% by
mass, polyfunctional)

Release agent b: UV Poly215: 0.10 parts by mass

Photo acid generating agent: Hexafluoroantimonate
triarylsulfonium salt: 0.10 parts by mass

(Product name: CPI (registered trademark) 101A,
active ingredient: 50% by mass, manufactured by San-Apro
Ltd.)

[0094]

(Example 8)

A release film for production of a super-thin layer
ceramic green sheet was obtained in the same manner as in
Example 1 except that the coating solution was changed to a
coating solution having a composition shown below.

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:

Celoxide (registered trademark) 2021P: 0.90 parts by
mass

Release agent b: UV Poly215: 0.10 parts by mass

Photo acid generating agent: Hexafluoroantimonate
triarylsulfonium salt: 0.10 parts by mass

(Product name: CPI (registered trademark) 101A,
active ingredient: 50% by mass, manufactured by San-Apro

Ltd.)

[0095]

(Example 9)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the coating solution was changed to a coating solution having a composition shown below.

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:

Celoxide (registered trademark) 2021P: 0.90 parts by mass

Release agent b: UV Poly215: 0.05 parts by mass

Acryloyl group-containing polyether-modified polydimethylsiloxane: 0.05 parts by mass

(Product name: BYK-UV3500, manufactured by BYK Chemie Japan, solid content: 100%)

Acid generating agent: UV CATA211 (active ingredient: 19% by mass): 0.26 parts by mass

[0096]

(Example 10)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the release agent b of Example 1 was changed to a long-chain alkyl group-containing release

agent obtained by the following preparation.

(Method for Preparing Long-Chain Alkyl Group-Containing Release Agent)

Stearyl acrylate and hydroxyethyl(meth)acrylate were mixed at a ratio of 95 mol% : 5 mol%, and the mixture was diluted with toluene such that the solid concentration was set to 40% by mass. To the diluted product, 0.5 mol% of azobisisobutyronitrile was added under a nitrogen stream, and the mixture was copolymerized to obtain a release agent A. The weight average molecular weight of the obtained polymer was 30,000.

[0097]

(Example 11)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the coating solution was changed to a coating solution having a composition shown below.

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:

Celoxide (registered trademark) 2021P: 0.90 parts by mass

Release agent b: Polydimethylsiloxane modified with epoxy at one end: 0.10 parts by mass

(Product name: X22-173DX, manufactured by Shin-Etsu

Chemical Co., Ltd., solid content: 100%)

Acid generating agent: UV CATA211: 0.26 parts by mass
[0098]

(Example 12)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the coating solution was changed to a coating solution having a composition shown below.

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:

Celoxide (registered trademark) 2021P: 0.90 parts by mass

Release agent b: perfluoro-based release agent: 0.10 parts by mass

Acid generating agent: UV CATA211 (active ingredient: 19% by mass): 0.26 parts by mass
[0099]

(Example 13)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that the coating solution was changed to a coating solution having a composition shown below.

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:
Celloxide (registered trademark) 2021P: 0.95 parts by
mass

Release agent b: UV Poly215: 0.05 parts by mass

Acid generating agent: UV CATA211 (active ingredient:
19% by mass):

0.26 parts by mass

[0100]

(Example 14)

A release film for production of a super-thin layer
ceramic green sheet was obtained in the same manner as in
Example 1 except that the coating solution was changed to a
coating solution having a composition shown below.

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:

Celoxide (registered trademark) 2021P: 0.80 parts by
mass

Release agent b: UV Poly215: 0.20 parts by mass

Acid generating agent: UV CATA211 (active ingredient:
19% by mass): 0.26 parts by mass

[0101]

(Example 15)

A release film for production of a super-thin layer
ceramic green sheet was obtained in the same manner as in

Example 1 except that the laminated film in Example 1 was changed to a laminated film X2 having a film thickness of 25 μm .

[0102]

(Example 16)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that coating was performed such that a film thickness of a release layer was set to 30 nm.

[0103]

(Example 17)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that coating was performed such that a film thickness of a release layer was set to 200 nm.

[0104]

(Example 18)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in Example 1 except that coating was performed such that a film thickness of a release layer was set to 0.8 μm .

[0105]

(Comparative Example 1)

A release film for production of a super-thin layer ceramic green sheet was obtained in the same manner as in

Example 1 except that the coating solution was changed to a coating solution having a composition shown below.

Methyl ethyl ketone: 49.43 parts by mass

Toluene: 49.43 parts by mass

Binder A containing cationically curable substance:

Celloxide (registered trademark) 2021P: 1.00 part by mass

Acid generating agent: UV CATA211 (active ingredient: 19% by mass): 0.26 parts by mass

[0106]

(Comparative Example 2)

A release film for production of a super-thin layer ceramic sheet was obtained in the same manner as in Example 1 except that a laminated film X1 was changed to a laminated film X3 (E5101-25 μm , manufactured by Toyobo Co., Ltd.). In E5101, both a surface layer A and a surface layer B contained inorganic particles, and the Sa of each of the surface layer A and the surface layer B was 24 nm.

[0107]

(Comparative Example 3)

A release film for production of a super-thin layer ceramic green sheet in the same manner as in Example 1 except that the coating solution was changed to a coating solution having a composition shown below, and coating was performed such that a film thickness of a release layer was

set to 0.8 μm .

Methyl ethyl ketone: 44.75 parts by mass

Toluene: 44.75 parts by mass

Binder containing photo-radically curable substance:

Dipentaerythritol hexaacrylate: 9.90 parts by mass

(Product name: A-DPH, manufactured by Shin-Nakamura
Chemical Co., Ltd., solid content: 100% by mass)

Release agent b: BYK-UV3500: 0.10 parts by mass

Photo-radical polymerization initiator:

Methyl-1-(4-methylthiophenyl)-2-morpholinopropane-1-
one: 0.50 parts by mass

(Product name: IRGACURE (registered trademark) 907,
manufactured by BASF, active ingredient: 100% by mass)

[0108]

[Table 1]

	Substrate film			Release layer				Acid generating agent		
	Type	Thickness (μm)	Surface roughness Sa (nm)	Binder A containing cationically curable substance	Release agent b		Type	Ratio of active ingredient of acid generating agent to total mass of binder A containing cationically curable substance and release agent b (parts by mass)		
					Ratio in release layer (%)	Type			Ratio in release layer (%)	
Example 1	X1	31	2	28	CEL2021P	90	UV Poly215	10	UV CATA211	5
Example 2	X1	31	2	28	CEL2021P/GT401 (95:5)	90	UV Poly215	10	UV CATA211	5
Example 3	X1	31	2	28	CEL2021P/GT401 (70:30)	90	UV Poly215	10	UV CATA211	5
Example 4	X1	31	2	28	CEL2021P/GT401 (50:50)	90	UV Poly215	10	UV CATA211	5
Example 5	X1	31	2	28	CEL2021P/OXT221 (95:5)	90	UV Poly215	10	UV CATA211	5
Example 6	X1	31	2	28	GT401	90	UV Poly215	10	UV CATA211	5
Example 7	X1	31	2	28	EHPE3150	90	UV Poly215	10	UV CATA211	5
Example 8	X1	31	2	28	CEL2021P	90	UV Poly215	10	CPI101A	5
Example 9	X1	31	2	28	CEL2021P	90	Poly215/BYK-UV3500 (50:50)	10	UV CATA211	5
Example 10	X1	31	2	28	CEL2021P	90	long-chain	10	UV CATA211	5

UV Poly215: Alicyclic epoxy group-containing polydimethylsiloxane

BYK-UV3500: BYK (registered trademark)-UV3500: Acryloyl group-containing polydimethylsiloxane

X22-173DX: Polydimethylsiloxane modified with epoxy at one end

UV CATA211: Photo acid generating agent

CPI101A: CPI (registered trademark) 101A: Photo acid generating agent

IRGACURE907: IRGACURE (registered trademark) 907: Photo-radical polymerization initiator (not acid generating agent)

[0109]

[Table 2]

	Thickness of release layer (μm)	Release layer surface roughness (nm)		Diiodomethane contact angle (°)				Peelability	Curl		Pinhole
		Sa	P	Initial θ_1	θ_2 after being immersed in toluene	Change in contact angle $ \theta_1 - \theta_2 $	<Evaluation>		Height (mm)	<Evaluation>	
Example 1	0.05	2	51	72.4	72.3	0.1	very good	1.4	0.5	very good	very good
Example 2	0.05	2	48	72.6	72.4	0.2	very good	1.0	0.5	very good	very good
Example 3	0.05	2	49	72.1	72.3	0.2	very good	1.3	0.5	very good	very good
Example 4	0.05	2	48	72.2	72.2	0.0	very good	1.4	0.5	very good	very good
Example 5	0.05	2	48	72.5	72.3	0.2	very good	1.1	0.5	very good	very good
Example 6	0.05	2	50	72.4	72.5	0.1	very good	1.6	0.5	very good	very good
Example 7	0.05	2	45	72.2	72.4	0.2	very good	1.3	0.5	very good	very good
Example 8	0.05	2	60	72.3	72.2	0.1	very good	1.6	0.5	very good	very good
Example 9	0.05	2	58	72.5	73.6	1.1	good	1.5	0.5	very good	very good
Example 10	0.05	2	48	62.2	62.0	0.2	very good	2.3	0.5	very good	very good
Example 11	0.05	2	47	67.7	67.0	0.7	very good	3.2	0.5	very good	very good
Example 12	0.05	2	50	65.3	65.1	0.2	very good	3.7	0.5	very good	good
Example 13	0.05	2	54	72.2	72.0	0.2	very good	1.9	0.5	very good	very good
Example 14	0.05	2	60	72.6	72.6	0.0	very good	0.9	0.5	very good	very good
Example 15	0.05	2	49	72.5	72.6	0.1	very good	1.4	1.5	good	good
Example 16	0.03	2	45	72.2	72.2	0.0	very good	2.0	0.5	very good	very good
Example 17	0.2	1	29	72.3	72.6	0.3	very good	1.5	1.5	very good	very good
Example 18	0.8	1	19	72.7	73.3	0.6	very good	1.4	2.5	good	good
Comparative Example 1	0.05	2	59	36.6	36.3	0.3	very good	-1)	0.5	very good	-1)
Comparative Example 2	0.05	21	410	72.4	72.5	0.1	very good	1.9	1.5	good	poor
Comparative Example 3	0.8	1	46	44.2	57.2	13.0	poor	4.3	12.0	poor	average

*1): Cannot be evaluated

INDUSTRIAL APPLICABILITY

[0110]

The release film for production of a ceramic green sheet of the present invention has a very smooth release layer surface, and a release layer is free from the possibility of being eroded by an organic solvent. This makes it possible to form a ceramic green sheet having a low peeling force and few defects such as pinholes even in an ultrathin layer having a thickness of 1 μm or less. By using a cationically curable substance having small curing shrinkage, a poor appearance such as curl is suppressed, which makes it possible to provide a release film for production of a ceramic green sheet which is free from the possibility of lowering the precision of electrode printing.

CLAIMS

1. A release film for production of a ceramic green sheet,
5 the release film comprising:
a polyester film including a surface layer **A** substantially containing no inorganic particles; and
a release layer provided on the surface layer **A**,
wherein the release layer is obtained by curing a
10 composition which contains a binder **A** containing a cationically curable substance, and one or more release agents **b**,
the binder **A** contains at least one cationically curable substance selected from a compound having an
15 alicyclic epoxy group in its molecule and a compound having an oxetane ring in its molecule, in which the number of cationically curable functional groups in the cationically curable substance is two or more, and
the binder **A** is contained in an amount of 80% by mass
20 or more based on a total solid content of the release layer.
2. The release film for production of a ceramic green sheet according to claim 1, wherein an absolute value of a difference between a diiodomethane contact angle θ_1 of a
25 release layer surface and a diiodomethane contact angle θ_2 of the release layer surface after being immersed in toluene is 3.0° or less.
3. The release film for production of a ceramic green
30 sheet according to claim 1 or 2, wherein at least one of

the release agents **b** is a compound having a silicone skeleton.

4. The release film for production of a ceramic green
5 sheet according to any one of claims 1 to 3, wherein at
least one of the release agents **b** is a polydimethylsiloxane
having at least one cationically curable functional group
selected from a glycidyl ether group, an alicyclic epoxy
group and an oxetane ring.

10

5. The release film for production of a ceramic green
sheet according to any one of claims 1 to 4, wherein the
release film has a release layer surface having average
area surface roughness (Sa) of 7 nm or less, and a maximum
15 protrusion height (P) of 100 nm or less.

20

6. The release film for production of a ceramic
green sheet according to any one of claims 1 to 5, wherein
the binder **A** further contains an acid generating agent.

7. The release film for production of a ceramic
green sheet according to any one of claims 1 to 6, wherein
the thickness of the release layer is 0.01 to 1.0 μm .

25 8. The release film for production of a ceramic
green sheet according to any one of claims 1 to 7, wherein
the average area surface roughness (Sa) of the surface
layer **A** is 7 nm or less.

9. The release film for production of a ceramic green sheet according to any one of claims 1 to 8, wherein the thickness ratio of the surface layer **A** is 20% or more and 50% or less of the total thickness of the polyester
5 film.

10. A method for producing a ceramic green sheet having a thickness of 0.2 μm to 1.0 μm , wherein the release film for production of a ceramic green sheet according to
10 any one of claims 1 to 9 is used.

11. A method for producing a ceramic capacitor, wherein the method for producing a ceramic green sheet according to claim 10 is employed.